

1043,616



# PATENT SPECIFICATION

DRAWINGS ATTACHED

1043,616

Date of Application and filing Complete Specification: March 3, 1964.  
No. 8872/64.

Application made in United States of America (No. 263417) on March 7, 1963.  
Application made in United States of America (No. 343207) on Feb. 7, 1964.  
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## COMPLETE SPECIFICATION

### Coated Filter Aid and improved Filtration method

— Furthermore relates to a

## ERRATUM

SPECIFICATION No. 1,043,616  
Amendment No. 1

Page 1, Heading, Index at acceptance, for  
C1(1E,1X) read C1 C(1E,1X)"

THE PATENT OFFICE  
21st October 1966

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- 25 characterized by having electronegatively charged surfaces. Filter aid materials are generally employed as a precoat layer on a filter screen or are added to a fluid suspension as a collector for suspended matter prior to introduction of the suspension to the filter chamber. 70
- 30 In accordance with the present invention there is provided a particulate filter aid material having an electronegatively charged surface at least partially coated with a water- 75
- 35 soluble polymer consisting of an alkylenimine polymer, a polyalkylene polyamine having a molecular weight of at least 1000, or a polymer of vinylbenzyltrimethyl ammonium chloride. Good results are obtained when the particulate filter aid contains from 0.01 to 0.5 weight percent of the polymer. Advantageously the particulate filter aid consists of diatomaceous earth, perlite, charcoal, sand, asbestos, cellulose pulp, fullers earth or mixtures thereof. 80
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- 45
- particular adapted to removing organic matter, organic matter of a mixture thereof from suspension and is particularly useful in removing micro-organisms from fluid media. The process of the invention is useful in removing suspended matter from liquid media for example, water, aqueous solutions, hydrophylic solvents or solutions, and from gaseous media for example, air. 85
- The coated filter aids of the present invention are advantageously characterized by high filtration rates, efficient filtration, i.e. low filtrate turbidity, and long filtration cycles. A periodic addition during filtration of small amounts of the coated filter aid to liquids to be filtered provides a further increase in the liquid filtration cycle length. In comparison with untreated filter aids, the coated filter aids of the present invention permit larger volumes of liquids to be filtered per unit time, longer periods of operation between cleaning and/or replacement of filter aid material and higher 90

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Int. Cl.:—C 09 c 1/00, C 09 c 1/28, C 09 c 1/42, C 09 c 1/44 // B 01 d, C 02 c

## COMPLETE SPECIFICATION

### Coated Filter Aid and improved Filtration method

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, 5 State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to coated filter aids and to a process for removing insoluble impurities from fluid media. More specifically, the invention concerns coated filter aid 10 materials which provide exceptionally efficient removal of dispersed or suspended materials present in fluids.

The filter aid materials of the invention are selected from a wide variety of materials 15 which are generally employed in particulate form for filtration purposes. A large majority of such filter aid materials are commonly referred to as anionic filter aids and are characterized by having electronegatively charged surfaces. Filter aid materials are generally employed as a precoat layer on a filter screen or are added to a fluid suspension 20 as a collector for suspended matter prior to introduction of the suspension to the filter chamber.

In accordance with the present invention there is provided a particulate filter aid material having an electronegatively charged surface at least partially coated with a water-soluble polymer consisting of an alkyleneimine polymer, a polyalkylene polyamine having a molecular weight of at least 1000, or a polymer of vinylbenzyltrimethylammonium chloride. Good results are obtained when the particulate filter aid contains from 0.01 to 0.5 weight percent of the polymer. Advantageously, the particulate filter aid consists of diatomaceous earth, perlite, charcoal, sand, asbestos, cellulose pulp, fullers earth or mixtures thereof.

The invention furthermore relates to a process for removing suspended materials from a fluid medium which comprises filtering the fluid medium through a layer of a particulate filter aid material having an electronegatively charged surface at least partially coated with a water-soluble polymer consisting of an alkyleneimine polymer, a polyalkylene polyamine having a molecular weight of at least 1000, or a polymer of vinylbenzyltrimethylammonium chloride.

In a modification of the process of the invention a slurry is formed of the fluid medium and at least a proportion of the particulate filter aid material and the slurry is subsequently filtered.

The filter aid material of the invention is thought to function not only as a means of increasing the surface of the filter medium but as a collector for suspended matter which because of its degree of dispersion would permit passage through many of the known filter media. The process of the invention is particularly adapted to removing inorganic matter, organic matter of a mixture thereof from suspension and is particularly useful in removing micro-organisms from fluid media.

The process of the invention is useful in removing suspended matter from liquid media for example, water, aqueous solutions, hydrophylic solvents or solutions, and from gaseous media for example, air.

The coated filter aids of the present invention are advantageously characterized by high filtration rates, efficient filtration, i.e. low filtrate turbidity, and long filtration cycles. A periodic addition during filtration of small amounts of the coated filter aid to liquids to be filtered provides a further increase in the liquid filtration cycle length. In comparison with untreated filter aids, the coated filter aids of the present invention permit larger volumes of liquids to be filtered per unit time, longer periods of operation between cleaning and/or replacement of filter aid material and higher

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- percentage removal of particle turbidity from the liquids filtered.
- The coated filter aid media of the present invention possess numerous cationic sites (i.e. sites having a positive charge) which are freely available to attract and hold particles bearing a negative surface charge. This "electrical trap" removal mechanism functions in addition to the less efficient physical entrapment mechanism (of untreated filter aids) which is apparently not impaired by the relatively thin cationic polyelectrolyte surface coating present on the treated filter aid.
- The more efficient and effective turbidity removal made possible by the freely available cationic sites of the coated filter aids allows the use of filter aid particles having diameters larger than is generally permissible when mechanical entrapment alone must be depended upon for turbidity removal in the filtration of liquids. This use of larger size filter aid particles results in larger "filtration channels" which make possible increased filtration rates and longer filtration cycles while maintaining efficient turbidity removal.
- The coated filter aid materials of the invention are prepared from anionic-type filter aid particles having an electronegatively charged surface, by forming a slurry of the filter aid in an aqueous solution of the cationic polymer or by tumbling particulate filter aid in a spray of dilute aqueous polymer solution. The slurry or spray treatment is normally followed by dewatering and drying of the resulting coated filter aid although the coating treatment may immediately precede the use of the coated filter aid in which case the wet, coated particles are merely deposited on a filter support. A concentration of from 1 to 15 weight percent of the polymer in aqueous solution is preferably employed to slurry or spray-treat the anionic filter aid. Advantageously from 0.01 to 0.5 weight percent of the coated filter aid product consists of the polyelectrolyte which forms an adherent surface layer bonded to the filter aid by the attraction of the oppositely charged materials. In the formation of this coating, only a very small portion of the cationic sites are neutralized by the bonding action leaving numerous freely available cationic sites to attract and hold negatively charged particles present in fluids passing through the filter bed. In order for this "electrical trap" phenomenon to be advantageously effective, it is necessary to select a cationic organic polymer which will furnish freely available cationic sites about the periphery of the coated filter aid particle.
- Cationic organic polymers which are especially efficacious for use in the treatment of anionic-type filter aids, to produce the coated filter aid materials of the present invention, are those prepared by the polymerization of an alkyleneimine, e.g. ethylenimine, to form an alkyleneimine polymer, and by the condensation reaction of a dihaloalkane with a polyalkylenepolyamine, e.g. ethylene dichloride and triethylenetetra-amine, to form higher molecular weight polyalkylenepolyamines. These polymers possess a high ratio of cationic charge sites to molecular weight and form aqueous solutions of the desired concentration for use in coating the anionic-type filter aids. Although these polymers are normally water-soluble, they form an adherent coating on the filter aid which is not removed by contact with water.
- A concentration of from about 5 to 30 weight percent of the cationic polyelectrolyte in aqueous solution is preferably employed as a stock solution to spraytreat the anionic-type filter aid. The more dilute solutions have a lower viscosity and are easier to use but result in the addition of more water to the filter aid. The water does not interfere with the performance of the coated filter aid, but the added weight due to water retained in the coated filter aid may be undesirable. When a filter aid slurry treatment procedure is employed the polymer concentration in the slurry is not critical. Many particular types of filter aids, such as diatomaceous earth, require large amounts of water to form a slurry. In their case, a solution containing 0.2 percent by weight or less of polymer is advantageous. More concentrated solutions may result in an excess of polymer being added merely to obtain sufficient liquid to obtain a slurry. This excess polymer will be lost when washing the coated filter aid, or during the filter cycle if the coated material is not washed, and therefore increases costs or results in filtrate contamination.
- Polymer concentrations less than 0.2 weight percent, e.g. in the range of 0.01 weight percent, may be used in the slurry if desired. Even more dilute solutions can be employed but this required handling large amounts of liquids in relation to the weight of filter aid coated since a polymer coating of from about 0.1 to 0.2 weight percent, based on the coated filter aid weight, is generally preferred.

#### EXAMPLE 1

The efficiency of untreated and polyelectrolyte coated filter aids in removing turbidity was studied in the following manner. A ball clay was used to prepare a contaminated water supply having 444 parts per million (hereafter ppm) turbidity as determined by optical measurements. Aliquots of this turbid water were then passed through 30 gram quantities of either untreated diatomaceous earth (DE) or coated diatomaceous earth in accordance with the invention contained on a 200 mesh nickel screen support encased in a vertical cylinder. The filter aid formed a bed of uniform depth over the cross-sectional area, 0.110 sq. ft., (102 cm.<sup>2</sup>) of the cylinder. A constant pressure head of 400 mm. Hg was

maintained during filtration.

In Table 1, below, the results of several such experiments are tabulated. Column (1) designates the filter aid precoat (DE or DE having an 0.1 weight percent coating of a specified polymer) and Column (2) lists the

effluent turbidity. In all cases a fixed amount of untreated DE was mixed with the influent to facilitate more rapid filtration of a total of 3 gallons (11.3 L) of contaminated water through the 30 grams of filter aid media forming the precoat.

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TABLE I

|   | (1) | (2)      |
|---|-----|----------|
| untreated diatomaceous earth (DE)<br>0.1 weight percent                       |     | 81.2 ppm |
| DE coated with ethylenimine polymer<br>(mol. wt. greater than about 100,000)  |     | 2.7 ppm  |
| DE coated with polyethylenepolyamine<br>(mol. wt. greater than about 100,000) |     | 4.7 ppm  |
| DE coated with polyvinylbenzyltrimethyl<br>ammonium chloride                  |     | 8.2 ppm  |

A similarly advantageous increase in turbidity removal is demonstrated when sand, charcoal, coal, paper filter pulp, fuller's earth and asbestos are treated with the listed polymers to yield a coated filter aid containing 0.1 weight percent of the polyelectrolyte.

#### EXAMPLE 2

The procedure of Example 1 was followed with the exception that the filtration was terminated when more than 45 minutes was required to filter one liter of turbid influent. When DE was treated with polyethylenimine (hereinafter PEI) or polyethylenepolyamine Polymer (hereinafter PEPA) to provide a filter aid having an 0.1 weight percent polymer coating, approximately 2.4 times as much liquid filtrate was collected, before the rate slowed to 45 minutes per liter, as when untreated DE was employed.

Those cationic organic polymers which furnish the largest numbers of freely available cationic sites when employed as a filter aid coating are preferred for use in the method of the present invention. The relative numbers of such freely available cationic sites on a coated filter aid can readily be determined by the procedure outlined below which establishes an "index" of the number of such sites. Indices determined by this method are correlated to filter cycle length and turbidity removal to establish the effectiveness of cationic polymers for use in coating anionic-type filter aids.

#### Procedure A

A high molecular weight anionic polyelectrolyte (a material corresponding to a copolymer of 30 mol percent sodium acrylate and 70 mol percent acrylamide and having a molecular weight of approximately 2,000,000) was pre-

pared employing carbon 14 to enable the use of tracer techniques in analytical determination. This polymer was of sufficiently high molecular weight to furnish molecules closely approximating the size of the anionic charge bearing impurities generally present in contaminated liquids subjected to filtration through filter air beds in clarification and purification procedures. The size of this polymer molecule ensured its reaction with only the freely available cationic sites of the polyelectrolyte coated filter aid which are equally available to colloidal and suspended anionic contaminants normally encountered in practical applications of filter aid media. The stock solution of tagged polyacrylamide was prepared to contain 10 parts per million of polymer.

A quantity of 10 ml. of a one weight percent aqueous solution of polyethylenepolyamine polymer (molecular weight about 200,000) was diluted to 500 ml. and employed to slurry 100 grams of DE filter aid (surface area = 4 meters<sup>2</sup>/gram; mean particle size = 23.8 microns). This was maintained for 30 minutes by employing a paddle agitator at 100 RPM to keep the DE in suspension. The slurry was then dewatered on a Buchner funnel, re-slurried with deionized water and dewatered as before to remove any excess polymer. This wash and dewatering step was repeated twice and the coated DE, having an 0.1 weight percent polymer coating was then dried on trays at ambient laboratory temperatures for 24 hours and bottled. Five aliquots of this dried, coated filter aid (0.25, 0.50, 0.75, 1.0 and 1.5 grams) were separately re-slurried with 50 ml. portions of the previously described stock solution of tagged anionic polyacrylamide for 15 minutes. A multi-paddle stainless steel agitator was employed at 100

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RPM in order to allow equilibrium adsorption conditions to be established. A low speed centrifuge was used to separate the coated filter aid and the liquid which was then decanted and analyzed by liquid scintillation counting techniques. Each sample was counted ten times with the average count per minute (cpm) related to the concentration (ppm) of tagged polyacrylamide. The data obtained are shown graphically in the accompanying drawing. The weight in grams of coated filter media (adsorbent) per gram of anionic polymer (adsorbate) sorbed was plotted against the reciprocal of the equilibrium concentration of the anionic polymer. This plot follows the well-known "Langmuir adsorption theorem" and is extrapolated to zero adsorbate concentration. The reciprocal of this zero adsorbate intercept denotes the grams of anionic polymer adsorbed per gram of coated filter media, or grams adsorbate/gram adsorbent. In the present case, the reciprocal of this zero intercept yields the weight in grams of anionic polymer adsorbed per gram of polyethylenepolyamine coated DE, which value provides an index of the number of freely available cationic sites present on the 0.1 weight percent polyethylenepolyamine coated filter media. Figure 2 illustrates the foregoing procedure which results in an index equal to 0.820 for the number of freely available cationic sites on the product. This index represents the number of grams of sorbed adsorbate per gram of adsorbent at zero solution concentration of the adsorbate.

This index of the number of freely available cationic sites can be obtained for any material employed as a filter aid coating at a given concentration as well as for various concentrations of each coating material present in the final product. In order to correlate indices obtained in this manner, for various cationic organic polyelectrolytes and other materials employed to coat filter aid media, with filtration characteristics, a "filtrability index" was established in the following manner.

#### Procedure B

"Filtrability indices," defined as the slopes of lines obtained by plotting the reciprocal of the rate of filtration (ordinate) versus the average volume of filtrate (abscissa) over a stepped time interval, were determined as in the following procedure illustrated by Figure 3.

A filter septum was covered with a precoat of thirty grams of DE and employed to filter an aqueous feed having five grams per gallon (3.79 l.) of suspended ball clay (Kaolinite-silica) impurity and 2.5 grams per gallon (3.79 l.) of DE having 0.2 weight percent polyethylenepolyamine coating. The filtration was carried out under constant pressure and the "filtrability index" ( $C_v$ ) was obtained from the slope of the line plot of data as in

Figure 3. Higher values of  $C_v$ , which indicate more rapid rate deceleration, are noted for filter aids coated with polyelectrolytes having lower indices of the number of freely available cationic sites. This is demonstrated in Figure 4 where filtrability index is plotted (ordinate) versus index of the number of freely available cationic sites for a number of polyelectrolytes employed to coat DE. In Figure 4 and Figure 5 explained below, the polyethylenepolyamine (PEPA) employed to coat DE had a molecular weight of more than 100,000 except where noted. Similarly, the polyethylenimine was of molecular weight greater than 100,000. The quaternary ammonium salt employed was of the alkyl trimethyl ammonium chloride and dialkyl dimethyl ammonium chloride type wherein the alkyl chains contain from 8 to 18 carbon atoms. The points on the Figures identified by the letters TMVB represent DE coated with a copolymer of acrylamide and vinylbenzyltrimethyl ammonium chloride.

The index of the number of freely available cationic charge sites is correlated to efficiency of turbidity removal in Figure 5 wherein the filtrate turbidity (initial influent turbidity = 444 ppm, optical measurement) is plotted in ppm on the ordinate and the cationic charge index is plotted as the abscissa. The kind and amount of coating on the DE filter aid is noted for each point.

#### EXAMPLE 3

A variety of bacteria were employed to contaminate sterile water samples and these samples were then passed through various filter media to test their capabilities for removing these microorganisms. Twenty-four hour broth cultures of *Escherichia coli*, *Staphylococcus albus* and *aureus*, alpha and gamma hemolytic *Streptococcus* and *Aerobacter aerogenes* were employed as the microorganisms in these tests. One ml. of a test culture was added to 100 ml. of sterile distilled water and total plate counts of the number of organisms present were determined by preparing serial dilutions.

The seeded samples were then filtered rapidly, under vacuum, through sterile Buchner funnels containing a filter bed of DE coated with (1) an ethylene imine polymer or (2) aluminum hydroxide. An untreated DE filter bed was used as a control. The coated DE was prepared by spraying the polymer as an approximately 15 weight percent aqueous solution onto the DE. The other polymer coatings were applied by the previously described slurry method. The aluminum hydroxide coated filter aid was prepared by forming an aqueous slurry of DE, aluminum sulfate and soda ash, agitating the slurry for 15 minutes, depositing the slurry on the filter support and washing with water to remove excess materials. The coated filter aid contained about 2 percent by weight of aluminum

hydroxide. The bacterial comparison counts Table II, below, of the influent and effluent are recorded in

TABLE II

| <i>DE filter aid</i>                     | <i>Microorganism</i>        | <i>Bacteria count per ml.</i> | <i>Pre-filtration</i> | <i>Post-filtration</i> |
|--|-----------------------------|-------------------------------|-----------------------|------------------------|
| untreated                                | <i>E. coli</i>              | 310,000                       | 210,000               |                        |
| 0.2 percent PEI <sup>(1)</sup>           | <i>E. coli</i>              | 17,000                        | 0                     |                        |
| untreated                                | <i>S. albus</i>             | 130,000                       | 88,000                |                        |
| 0.2 percent PEI <sup>(1)</sup>           | <i>S. albus</i>             | 76,000                        | 0                     |                        |
| 2 percent Al(OH) <sub>3</sub>            | <i>S. albus</i>             | 7,300                         | 60                    |                        |
| 0.2 percent PEI <sup>(1)</sup>           | <i>α-Streptococcus</i>      | 5,000                         | 0                     |                        |
| 0.2 percent PEI <sup>(1)</sup>           | <i>Aerobacter aerogenes</i> | 490,000                       | 0                     |                        |
| 1.0 percent polyazetidine <sup>(2)</sup> | <i>Aerobacter aerogenes</i> | 50,000                        | 0                     |                        |

<sup>(1)</sup> PEI ethyleneimine polymer

<sup>(2)</sup> polyazetidine—polymeric N,N-diethyl-3-hydroxy-azetidine.

- 5 Although the inorganic coated DE produced a marked reduction in bacterial count, the rapid growth rates of bacteria make the presence of even a very few bacteria intolerable when sterile effluent is desired.

#### EXAMPLE 4

- 10 Filtering grade sand, about 0.5 mm diameter, was soaked for 12 hours in an aqueous 0.5 weight percent PEI solution to establish equilibrium. All excess PEI was then washed off with deionized water and an 15 18 inch (45.7 cm.) high column of this treated sand was placed in a 36 inch (91.4 cm.) vertical glass tube having a diameter of 1 inch

(2.5 cm.). All equipment was sterilized by autoclaving prior to addition of the coated sand. The sand was fluidized by a back-wash 20 with sterile water and then allowed to settle with an inch of water above the sand level. The feed consisted of 700 mls. of sterile water inoculated with *Escherichia coli* and was filtered at a gravity rate of 30 ml. per minute. Serial dilutions of the prefiltrate and post filtrate were employed to determine total bacterial population. Untreated sand and sand coated with aluminum hydroxide were employed in otherwise identical runs for the purpose of comparison. Table III, below, is a compilation of the results obtained. 25 30

TABLE III

| <i>Filter media</i>                  | <i>Bacterial Count per ml.</i> | <i>Pre-filtration</i> | <i>Post-filtration</i> |
|--------------------------------------|--------------------------------|-----------------------|------------------------|
| untreated sand                       | 80,000                         | 69,000                |                        |
| untreated sand                       | 86,000                         | 50,000                |                        |
| sand coated with Al(OH) <sub>3</sub> | 19,000                         | 20                    |                        |
| sand coated with PEI                 | 82,000                         | 0                     |                        |

Once again the significance of the results resides in the necessity for complete removal of bacteria since even the relatively small numbers allowed to pass through into the filtrate by the aluminum hydroxide coated sand are capable of rapid growth and rebuild-up of the bacterial population.

Total removal of intestinal parasites by filtration through 0.6 mm. sand, coated using the same technique as described above, at rapid filtration rates was also accomplished. *Endoameba hislopytica*, *Endolimax nina* and *Enterobius vermicularis* were used to inoculate a sterile water influent. Total removal of these microorganisms was observed at a flow rate of 2 gallons per minute per square foot of filter area.

#### EXAMPLE 5

The removal of microorganisms from a variety of liquids was demonstrated with DE having an 0.2 weight percent PEI coating employed as the filter media. Beer containing 400 microorganisms per ml. was filtered at a rate of a liter/min. through a No. 2 Buchner funnel containing a  $\frac{1}{4}$  inch (0.63 cm.) thick layer of the coated filter aid with complete removal of the microorganisms being observed. In a similar manner, kerosene contaminated by 130,000 microorganisms/ml. was sterilized by passage through this coated filter aid medium with no blinding or plugging of the filter media.

#### EXAMPLE 6

The following experiment was conducted to demonstrate the effectiveness of the present method to remove viral organisms from fluids. In a series of runs, 10.0 gram quantities of coated diatomaceous earth, having 0.2 weight percent PEI was slurried with 100 ml. of a standard nutrient medium containing 0, 5, 10, or 20 weight percent horse serum. Each such slurry was filtered through a filter paper in a Buchner funnel to form a filter bed and portions of the filtrate were tested in established monolayer tissue cultures of bovine kidney tissue. No evidence of toxicity of such filtrates to the tissue cultures was observed. Immediately after filtering the nutrient medium to

form the filter bed, 100 ml. of a suspension of infectious bovine rhinotracheitis virus, hereafter IBR, was passed through the filter bed. Serial dilutions of the filtrate from each filter bed were inoculated into tubes containing cultures of bovine kidney established cells. The cultures were then incubated under good growing conditions and observed for the development of the characteristic cytopathological effect indicative of the presence of IBR virus. The suspension of IBR virus employed as starting material represented harvests from tissue cultures of the virus which had been pooled to provide 500 ml. of a suspension which assayed  $10^{3.5}$  tissue culture infectious doses — 50 percent, hereafter TCID<sub>50</sub>, of IBR virus per 0.2 ml. The value is determined from that dilution at which there is a cytopathogenic effect observed in 50 percent of the culture tubes inoculated with said dilution. The results of these experiments showed no cytopathogenic effect when corresponding assays were carried out with the filtrates from the coated filter aid beds which had been prepared from slurries containing 0, 5, 10 and 20 weight percent horse serum.

#### EXAMPLE 7

The effectiveness of the method of the present invention in removing microorganisms from commercially employed dry cleaning solvents was tested by inoculating a 1 : 1 weight ratio, tetrachloroethylene : water solution, with various bacteria and then filtering the contaminated solution through forty grams of DE having an 0.2 weight percent of PEI. A standard No. 2 Buchner funnel was employed. The dilution of the dry cleaning solvent was necessary since 100 percent tetrachloroethylene is toxic to the bacteria employed. The coated DE was prepared by spray-treatment of DE with an aqueous solution of PEI. The tetrachloroethylene-water suspensions of the test organism were filtered and the number of bacteria present before and after filtration were enumerated by standard plate counts. After 24 hours incubation at 37°C. counts of bacteria were obtained as listed in Table V, below, in number of bacteria/ml.

TABLE V

| <i>CCl<sub>2</sub>CCl<sub>2</sub>-H<sub>2</sub>O<br/>Suspension</i> | <i>Untreated DE</i>   |                        | <i>Bacteria/ml.</i>   |                        |
|---|-----------------------|------------------------|-----------------------|------------------------|
|   | <i>Pre-filtration</i> | <i>Post-filtration</i> | <i>Pre-filtration</i> | <i>Post-filtration</i> |
| <i>A. aerogenes</i>   | 16,000                | 8,000                  | 14,000                | 0                      |
| <i>S. aureus</i>  | 17,000                | 3,000                  | 8,000                 | 0                      |
| <i>B. subtilis</i>  | 19,000                | 2,000                  | 20,000                | 0                      |

**EXAMPLE 8**

5 The capacity of PEI treated DE to remove microorganisms from air by filtration was demonstrated by placing a dry filter medium, consisting of DE spray-treated with PEI to prepare a coated filter aid having 0.2 weight percent PEI, in a No. 2 Buchner funnel with a No. 2 Whatman filter paper used to support the coated filter aid. This filter was then connected by means of a cored rubber stopper to

15 a nitro-cellulose ester membrane filter. The system was brought to vacuum and the flow rate controlled at 600 liters/hr. Upon completion of a filtration run, the membrane filter (0.45 micron pore size) was cultured on Standard Methods Agar and the microorganisms enumerated. The results in total bacteria and fungi present at various time intervals is listed in Table VI, below.

TABLE VI

| <i>Filter media</i>                  | <i>Time (min.)</i> | <i>Bacteria-Fungi Count</i> |
|--------------------------------------|--------------------|-----------------------------|
| none                                 | 15                 | 24                          |
| none                                 | 30                 | 42                          |
| none                                 | 60                 | 63                          |
| untreated DE                         | 15                 | 13                          |
| untreated DE                         | 30                 | 29                          |
| untreated DE                         | 60                 | 54                          |
| 0.2 weight percent PEI coating on DE | 15                 | 0                           |
| "                                    | 30                 | 0                           |
| "                                    | 60                 | 0                           |

**EXAMPLE 9**

20 The following experiment was conducted to determine the effectiveness of the filter aid coating in preventing the growth of microorganisms through the filter bed.

25 Diatomaceous earth was slurried with an 0.2 weight percent aqueous solution of the polyalkylenopolyamine of Example 1, having an average molecular weight of 400, and formed into an approximately  $\frac{1}{2}$  inch thick

30 filter bed in a standard Buchner funnel. The funnel was connected to a 500 ml. filter flask containing 100 ml. of sterile nutrient broth

35 and successive portions of a heavily bacteria-contaminated water were filtered through the coated filter medium over a three day period. Any turbidity occurring in the nutrient broth was indicative of bacterial growth, in this case due to bacterial "grow through," since the starting system was sterile, the only access to the broth was through the filter media, and the coated filter aid removed all bacteria from the contaminated solution being filtered. An untreated DE filter bed was employed as a control. The results are tabulated in Table VII, below.

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TABLE VII

| <i>Time (hrs.)</i> | <i>Untreated DE</i> | <i>Coated DE</i> |
|--------------------|---------------------|------------------|
| 16                 | visible growth      | no growth        |
| 24                 | "                   | "                |
| 48                 | "                   | "                |
| 72                 | "                   | "                |

**WHAT WE CLAIM IS:—**

1. A particulate filter aid material having an electronegatively charged surface at least partially coated with a water-soluble polymer consisting of an alkyleneimine polymer, a polyalkylene polyamine having a molecular weight of at least 1000, or a polymer of vinylbenzyltrimethyl ammonium chloride.
2. A particulate filter aid material as claimed in Claim 1 containing from 0.01 to 0.5 weight percent of the polymer.
3. A particulate filter aid material as claimed in Claim 1 or Claim 2 wherein the alkyleneimine polymer is an ethylenimine polymer.
4. A particulate filter aid material as claimed in any one of claims 1, 2 or 3 which consists of diatomaceous earth, perlite, charcoal, sand, asbestos, cellulose pulp, fullers earth or mixtures thereof.
5. A process for removing suspended materials from a fluid medium which comprises filtering the fluid medium through a layer of a particulate filter aid material having an electronegatively charged surface at least partially coated with a water-soluble polymer consisting of an alkyleneimine polymer, a polyalkylene polyamine having a molecular weight of at least 1000, or a polymer of vinylbenzyltrimethyl ammonium chloride.
6. A modification of the process claimed in Claim 5 which comprises forming a slurry of the fluid medium and at least a proportion of the particulate filter aid material and subsequently filtering the slurry.
7. A process as claimed in Claim 5 or Claim 6 wherein the coated filter aid employed
- contains from 0.01 to 0.5 weight percent of the water-soluble polymer.
8. A process as claimed in any one of claims 5, 6 or 7 wherein the suspended materials in the fluid medium consist of or contain inorganic matter, organic matter or a mixture thereof.
9. A process as claimed in any one of claims 5 to 8 wherein the suspended matter in the fluid medium contains microorganisms.
10. A process as claimed in any one of claims 5 to 9 wherein the fluid medium is a liquid.
11. A process as claimed in Claim 10 wherein the liquid is water.
12. A process as claimed in any one of claims 5, 7, 8 or 9 wherein the fluid medium is a gas.
13. A process as claimed in Claim 12 wherein the gas is air.
14. A method of preparing the particulate filter aid material according to Claim 1 substantially as hereinbefore described with reference to the Examples.
15. A particulate filter aid material as claimed in Claim 1 substantially as described with reference to the specific Examples.
16. A process for removing insoluble suspended materials from a fluid medium as claimed in Claim 6 substantially as described with reference to the specific Examples.

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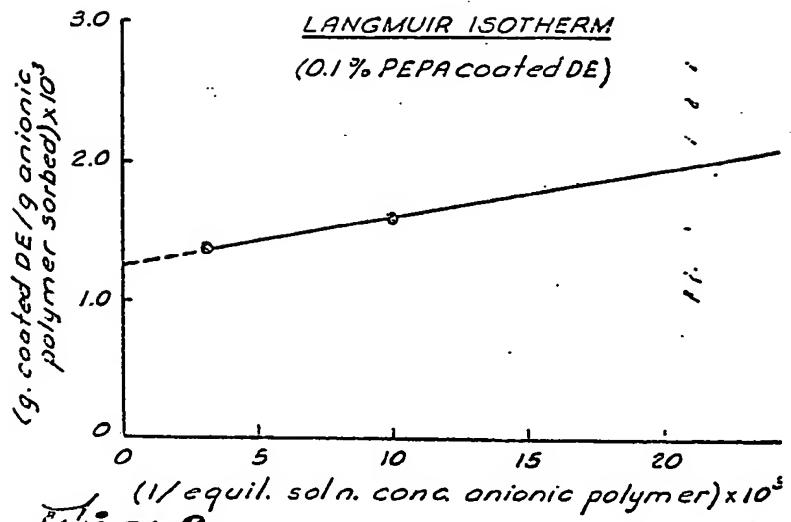


Fig. 2

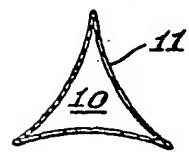
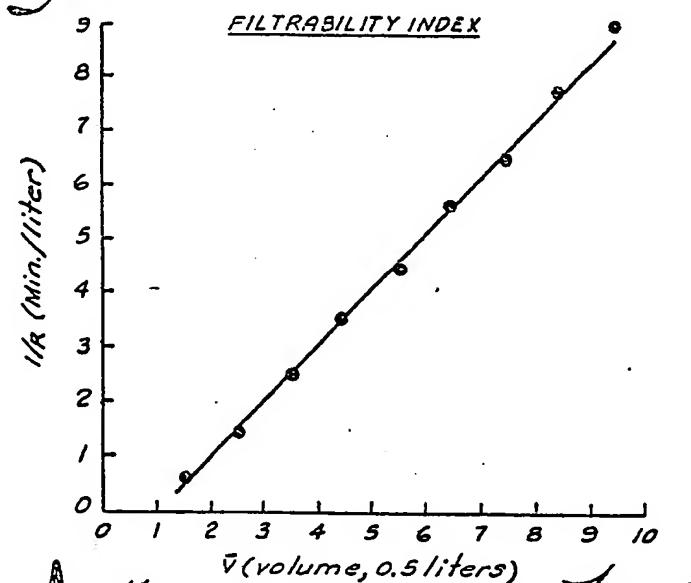


Fig. 1

Fig. 3

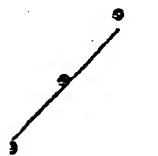
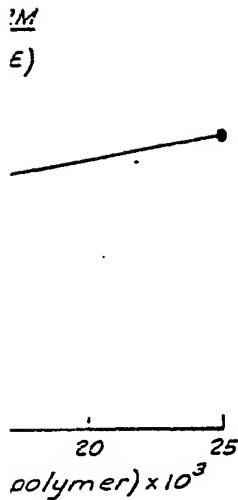
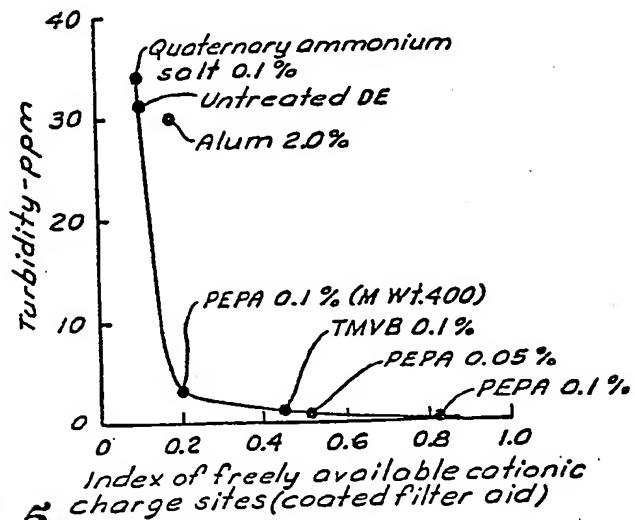
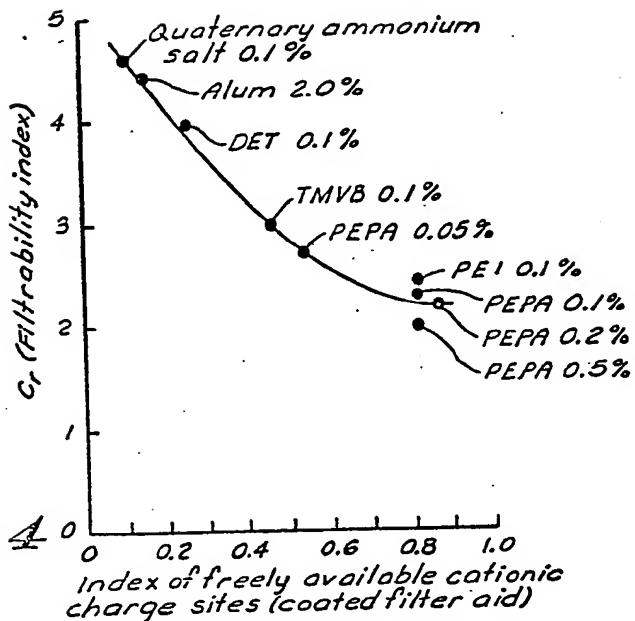


Fig. 3



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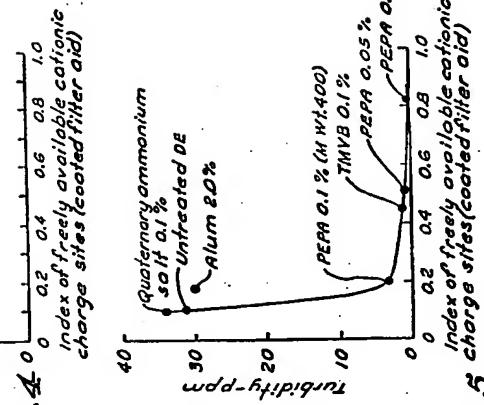
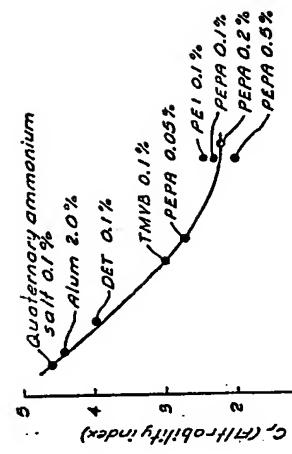
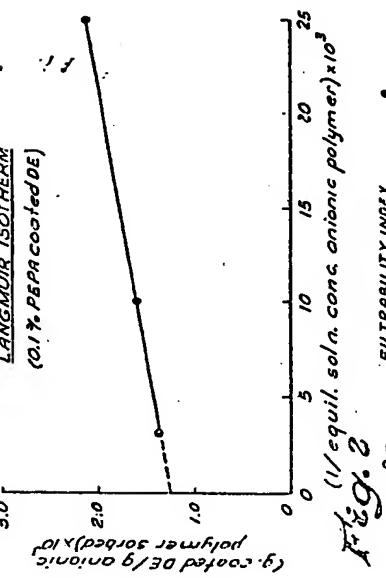


Fig. 3

Fig. 1

Fig. 5

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